

ATODP0100US

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :
: Group Art Unit: 1763
Feurhapter et al :
Serial No.: 10/675,019 : Examiner: Roberts P. Culbert
: Confirmation No. 4826
Filed: September 30, 2003 :
For: IMPROVED METHOD FOR MICRO-ROUGHENING TREATMENT OF COPPER
AND MIXED-METAL CIRCUITRY

DECLARATION OF PATRICK P. BROOKS UNDER 37 C.F.R. 1.132

**VIA EFS
M/S AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450**

Sir:

I, Patrick P. Brooks, declare and say as follows:

(1) I am a named inventor on the above-identified application. I am an employee of Atotech Deutschland GmbH ("Atotech"), the assignee of the above-identified application. At present, I am Product Manager for Surface Treatment Technologies at Atotech. I worked as an R&D chemist in the area of PCB manufacturing research and development at Atotech, particularly in the area of surface treatment, etching, plating of metal layers and lamination of the metal layers to dielectric materials for five years. I hold a bachelor's degree in chemistry from the

University of Illinois at Chicago (1996). I have been employed in the area of printed circuit board R&D and manufacturing for over 11 years, including 4 years at a PCB manufacturing company and seven years at Atotech. I am the author or co-author of several PCB-related technical papers and, in addition to the present application, am a co-inventor on several recently-filed German patent applications. For these reasons and with this background, I consider myself and believe I am considered by my colleagues to be a person of skill in the art of printed circuit board manufacture, particularly with respect to metal substrates and in the area of surface micro-roughening and intergranular etching of such substrates.

(2) The present application discloses and claims a process to improve the adhesion of dielectric materials to a metal layer, and includes a step of providing an unpatterned metal layer having a first major surface, in which the metal layer includes a layer of copper and a layer of a second metal or alloy. An example of this "mixed-metal" is copper-invar-copper, also known as CIC. The process further includes a step of micro-roughening the first major surface to form a micro-roughened surface. This micro-roughening removes some metal, roughens the surface, increases the surface area, and prepares the surface for later bonding to dielectric materials. The process further includes a step of etching the metal layer to form a circuit pattern in the metal layer and, in accordance with this process, the micro-roughening is carried out prior to the etching. This temporal relationship is important because, in a mixed-metal layer, if the micro-roughening is carried out subsequent to the circuit pattern-forming etching step, due to galvanic edge effects arising from the two different metals in close proximity to each other, the entire surface may not be micro-roughened, thereby resulting in inferior adhesion to the subsequently applied dielectric materials. That is, the galvanic edge effect, discovered by the present inventors and addressed by this invention, would result in little or no roughening of the surface of the circuit pattern formed from a mixed-metal substrate. In accordance with one embodiment of the

process, the micro-roughening is carried out by applying a mixture comprising water, acid, an oxidant and a corrosion inhibitor to the unpatterned metal layer. This combination results in effective micro-roughening of the surface. In this process, the surface area of the first major surface is increased by a factor of from about 60% to about 120% in the micro-roughening step. That is, in the present inventive process, a small but significant amount of metal is removed from the surface of the metal in the micro-roughening step, and the surface undergoes a significant but controlled increase in surface area and roughness.

(3) It is my understanding that the claims of the present application have been rejected over various combinations of prior art. First it is my understanding that the USPTO examiner contends that it would have been obvious to use the roughening treatment disclosed in U.S. Patent No. 6,261,466 B1, to Bayes et al. ("Bayes") as a replacement for the black oxide treatment of a metal surface disclosed in U.S. Patent No. 6,500,349 B2, to Andresakis et al. (referred to below as "Andresakis"), in roughening the surface of a mixed-metal layer such as disclosed in U.S. Published Application No. 2002/0029730, to Lee et al. ("Lee"), and that having done this, a process the same as the presently claimed invention would have been obtained and that it would have been obvious to make these combinations, as a result of which the Examiner asserts the presently claimed invention would have been obvious and is therefore unpatentable.

(4) As a person of skill in the art, I disagree with the Examiner's position, because each of these treatments results in the formation of a different surface and neither the process of Andresakis nor the process of Bayes, if applied to the same initial surface, would result in the same roughened surface as that obtained in the presently claimed invention. In December, 2006, I carried out a series of tests to prove this point, discussed in the following.

(5) I have conducted a series of tests designed to compare and contrast the results of treatment of a copper metal surface with the black oxide taught by Andresakis, the roughening treatment taught by Bayes and the micro-roughening treatment taught by the present invention and claimed in the present application.

(6) In the following, R_a is the average of the absolute values of the surface height measured from the mean data plane. R_{ms} is the Root Mean Square of height deviation as measure from the mean data plane. R_z is the difference from the highest 10 peaks and the lowest 10 valleys. %RSAI is percentage Relative Surface Area Increase, which is a theoretical increase in the surface area within a known area, and is calculated from R_a , R_{ms} and R_z . This is the surface area increase referred to in the present application and which I understand is now specifically recited in the pending claims.

(7) In carrying out the following experiments, the process steps outlined were used. For the black oxide, the standard treatment as known in the art was used. For both the Bayes process and the process in accordance with an embodiment of the present invention, the procedure outlined below was used. Thus, for the Bayes and present invention samples, all of the steps were the same, except for the composition used in the "adhesion promotion" step of Bayes and in the micro-roughening step of the present invention. When the Bayes chemistry was used, the etch depth obtained was $2.75\text{ }\mu\text{m}$ for a two minute immersion (as per Examples 1-3 of Bayes), while with the chemistry of the present invention, the etch depths obtained were $0.8\text{ }\mu\text{m}$ for a one minute immersion and $1.6\text{ }\mu\text{m}$ for a two minute immersion. BTA is benzothiazole, ATA is aminothiazole, IPGA is isopropyl glycol alcohol (ethylene glycol mono isopropyl ether) and TMAH is tetramethylammonium hydroxide. The conditions are shown below:

The Black Oxide parameters were as follows:

	<u>Chemical Treatment</u>	<u>Components</u>	<u>Temp</u>	<u>Immersion Time</u>
Step 1	Alkaline Cleaner	Sodium Hydroxide	50°C	4 minutes
Step 2	Rinse	DI Water	RT	1 minute
Step 3	MicroEtch	50 g/l Sodium Persulfate 92 g/l H ₂ SO ₄	30°C	1 minute
Step 4	Rinse	DI Water	RT	1 minute
Step 5	Pre-Dip	Sodium Hydroxide (10 g/l)	35°C	2 minutes
Step 6	Oxide Bath	Sodium Hydroxide (10 g/l) Sodium Chlorite (152 g/l)	70°C	5 minutes
Step 7	Rinse & Dry	DI Water	RT	1 minute + dry

The Bayes parameters were as follows:

	<u>Chemical Treatment</u>	<u>Components</u>	<u>Temp</u>	<u>Immersion Time</u>
Step 1	Acid Clean	Phosphoric/Citric acid	40°C	2 minutes
Step 2	Rinse	DI Water	RT	1 minute
Step 3	Alkaline cleaner	Glucanate/NaOH	55°C	2 minutes
Step 4	Rinse	DI Water	RT	1 minute
Step 5	Activator	1 g/l BTA 50 ml/l IPGA	35°C	45 seconds
Step 6	Bayes	6.8 g/l	35°C	2 minutes
	Ex. 1-3	170 ml/l H ₂ SO ₄ (50%)		
	US 6054061	35 ml/l H ₂ O ₂ 100, 500, 2500 mg/l TMAH Balance DI water to 1 liter		
Step 7	Rinse & Dry	DI Water	RT	1 minute + dry

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The present invention parameters were as follows:

	<u>Chemical Treatment</u>	<u>Components</u>	<u>Temp</u>	<u>Immersion Time</u>
Step 1	Acid Clean	Phosphoric/Citric acid	40°C	2 minutes
Step 2	Rinse	DI Water	RT	1 minute
Step 3	Alkaline cleaner	Glucanate/NaOH	55°C	2 minutes
Step 4	Rinse	DI Water	RT	1 minute
Step 5	Activator	1 g/l BTA	35°C	45 seconds
		50 ml/l IPGA		
Step 6	Present	10 g/l BTA	35°C	1 minute 0.8 µm
	Invention	92 g/l H ₂ SO ₄		2 minute 1.6 µm
		0.8 g/l ATA		
		35 ml/l H ₂ O ₂		
		Balance water to 1 liter		
Step 7	Rinse & Dry	DI Water	RT	1 minute + dry

(8) When these processes were applied to a copper metal surface, the following results were obtained:

<u>Treatment</u>	<u>Surface Change</u>	<u>R_a</u>	<u>R_{ms}</u>	<u>R_z</u>	<u>%RSAI</u>
Black Oxide	0.4 mg/cm ² added	315 nm	458 nm	3.21µm	148%
	0.65 mg/cm ² added	325 nm	429 nm	3.48µm	188%
Bayes	2.75 µm removed	252 nm	320 nm	3.02 µm	15.8%
	2.75 µm removed	230 nm	288 nm	2.16 µm	39.8%
	2.75 µm removed	188 nm	235 nm	1.63 µm	43.6%
Present	0.8 µm removed	274 nm	343 nm	2.32 µm	75.3%
Invention	0.8 µm removed	249 nm	310 nm	1.94 µm	97.0%
	1.6 µm removed	397 nm	488 nm	3.14 µm	99.6%
	1.6 µm removed	354 nm	438 nm	2.60 µm	117.5%

(9) As shown by the foregoing, the black oxide process disclosed by Andresakis, the oxidation process disclosed by Bayes, and the micro-roughening process of the present application, result in the formation of a substantially different surface from each other. As is quite clear from the above experimental results, if the process disclosed by Bayes is used in place of the black oxide process taught by Andresakis, a surface such as that disclosed and claimed in the present application would not be obtained, even if all the other variables are constant. As shown by the foregoing, the black oxide actually adds weight to the surface, and does not substantially remove metal (although atoms of copper metal may be removed, be oxidized and then be replaced on the surface as copper oxide). Despite removing little or no metal from the surface, the black oxide process disclosed by Andresakis increases the roughness of the surface by a much greater degree than do either the process disclosed by Bayes or the process of the present invention. Conversely, despite the fact that it removes much metal from the surface, the process disclosed by Bayes increases the surface area by much less than do either the process disclosed by Bayes or the process of the present invention. Finally, the process of the present invention provides a surface area increase in a range between the two extremes offered by either Bayes on the low side or the black oxide of Andresakis on the high side, while removing an amount of metal greater than Andresakis but less than Bayes.

(10) Finally, based on the foregoing evidence, it is clear to me as a person of skill in the art that, even if the roughening process of Bayes would be used to treat the surface of an unpatterned metal layer, by substituting the process of Bayes for the initial roughening step of Andresakis, where the unpatterned metal layer includes a layer of copper and a layer of a second metal or alloy, that the presently claimed invention would not be obtained. This is so at least because the increase in the surface area would not be within the range set forth in the presently pending claims. That is, all of the features of the claimed invention would not be obtained by the combination of prior art references, as contended by the Examiner in the present application.

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I, Patrick P. Brooks, hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued therefrom.

Respectfully submitted,



Patrick P. Brooks

28.02 07

Date